Pressure Broadening as a Test of Collision Rates Final Report

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A. Introduction

The results described here were carried out under the monitorship of the late Sheldon Green, whose sudden passing away has saddened all of us. I shall miss his ebullient sense of humor, as we all shall, and the intellectual stimulation provided by his large interests and expertise in scientific matters. Mostly, we will just miss him. The two sections following this one owe their genesis to suggestions and questions brought up by Dr. Green, and the last section of results is a natural outgrowth of the third section. Now that I am retired, I plan to extend these investigations at my leisure and eventually to publish them. I thought, however, that in the mean time NASA should have a short description of whatever I have managed to accomplish during the period of the grant awarded to me while I was still at JHU/APL. Dr. Green had seen most of these results piecemeal as they came out.

B. Extension of GHM to Asymmetric Tops and Diatomic Molecules

GHM, the Generalized Hess Method,[1,2,3] had been worked out in detail to line shape calculations in mixtures of diatomic and diatomic and/or monatomic molecules and applied several times,[4,5] the most successfull application being the prediction of absorption line shapes in HF-argon mixtures.[6] The extension to non-linear molecules had been left to future investigations and it was one of the goals of this project to work out the implications of an extension based on an approximation used successfully in other applications by Sheldon Green.[7] This is simply to assume that the quantum

numbers for the rotation about the figure axis are good quantum numbers in molecular scattering calculations, this rotational degree of freedom acting mainly as a spectator to the collision as far as the angular momentum coupling is concerned. The scattering wave function for symmetric top-atom collisions can then be expanded in sums of total angular momentum wave functions,

$$\mid JMjk\ell\rangle = \sum_{m,m_\ell} \langle jm\ell m_\ell \mid JM\rangle \mid jkm\rangle \mid \ell m_\ell\rangle,$$

which can be regarded as a representative member of a complete set. $\mid jkm\rangle$ is a rotation wave function, $\mid \ell m_\ell\rangle$ the orbital angular momentum wave function and $\langle .... \mid ..\rangle$ a Clebsch-Gordan coefficient.[8] The extension to asymmetric tops can then carried out by expanding the asymmetric top wavefunction in symmetric top wave functions:

$$\mid jm\tau\rangle = \sum_k a_{\tau k} \mid jkm\rangle$$

$$\sum_m a_{\tau m} a^*_{\tau' m} = \delta_{\tau\tau'}.$$

This can be extended to top-diatomic molecule collisions by the replacement,

$$\mid jkm\rangle \longrightarrow \mid j(j_T j_D)km\rangle = \sum_{m_T m_D} \langle j_T m_T j_D m_D \mid jm\rangle \mid j_T k m_T\rangle \mid j_D m_D\rangle.$$

Formally, the extension of this model to the GHM line shape formulae is almost trivial. The GHM collision integrals[2,3] take the form

$$\begin{aligned} \left\langle \mathbf{X}'^{\dagger}\mathbf{L}\mathbf{X}\right\rangle &= tr\mathbf{X}'^{\dagger}\mathbf{L}\mathbf{X} \\ &= \sum_{\widetilde{jkm}} \left\langle \widetilde{jkm} \mid \mathbf{X}'^{\dagger}\mathbf{L}\mathbf{X} \mid \widetilde{jkm}\right\rangle \end{aligned}$$

where $\mathbf{L}$ is a collision "superoperator" or "tetradic", $\mathbf{X}^\dagger$ is the adjoint of the operator $\mathbf{X}$, and $\mathbf{X}$ has the form either of $\mathbf{TV}$ or $\mathbf{T}$ where $\mathbf{V}$ is a molecular velocity and $\mathbf{T}$ is one of a set of operators useful for describing the dipole moment of molecular radiative transitions:

$$\mathbf{T}^{qn}_{jk,j'k'} = \mu_{jk\widetilde{\alpha},j'k'\widetilde{\alpha}'} \sum_{mm'} \mid jkm\rangle \imath^q (2q+1)^{1/2} (-1)^{j-m} \begin{pmatrix} j & q & j' \\ m & n & -m' \end{pmatrix} \langle j'k'm' \mid ..$$

where (:::) is a Wigner 3-j symbol.[8] This is a slight extension of the set of operators introduced previously[3,6] and assumes explicitly that the role of the figure axis quantum number, k, in the angular momentum coupling is that of a spectator. In actual transitions, the line strength and selection rules will be governed by the Hönl-London

factors,[8] which are functions of k and k'. μ is a dipole moment matrix element incorporating the Hönl-London factors and $\tilde{\alpha}, \tilde{\alpha}'$ are the quantum numbers for the other degrees of freedom - vibrational, electronic, nuclear - which are also assumed here to act as spectators to the angular momentum coupling. Since the potential energy matrix may depend on $\tilde{\alpha}k$ and $\tilde{\alpha}'k'$ parametrically, the t-matices will do so too. A glance at section IIIC of Monchick[3] shows that the couple $\tilde{\alpha}k$ plays the same role in GHM theory as the quantum number sets α_1 and α_2, and so all the formulae of that section can now be carried over immediately and applied to symmetric and asymmetric top line shapes with little or no change. The time required to calculate the t-matrices will be lengthened by the extra parameters introduced by the extra degrees of freedom but not the size of the calculations themselves. Consequently, a calulation such as the one carried out for HF-argon mixtures is feasible for H_2O-H_2 and H_20-CO mixtures, systems of astrophysical interest. Systems of interest in climate physics that could be handled in this way are N_2-H_2O and O_2-H_2O.

C. Off-Energy-Shell collisions by the Sams-Kouri Method

For the calculation of isolated line shapes, scattering calculations on the energy shell seem to be sufficient.[4,5,6] However, for overlapping lines[9] and apparently for the far wings of isolated lines,[10] the Fano tetradic[11] form of **L**, which is framed in terms of off-energy-shell t-matrices, must be used. The t-matrix is defined by

$$t_{i\mathbf{k}i'\mathbf{k}'}(E) = \langle i\mathbf{k} \mid \mathbf{V} \mid i_0\mathbf{k}_0; E\rangle^+$$

where, according to the Lippmann-Schwinger equation,

$$(E - \mathbf{H}_0 - \mathbf{V}) \mid i_0\mathbf{k}_0; E\rangle^+ = (E - \mathbf{H}_0) \mid i_0\mathbf{k}_0\rangle,$$

$\mathbf{H}_0$ is the free particle hamiltonian in the center of mass coordinate frame, $\mathbf{V}$ is the potential energy of interaction, $\mid i_0\mathbf{k}_0; E\rangle^+$ is the outgoing scattering wave function corresponding to the initial state

$$\langle \mathbf{r} \mid i_0\mathbf{k}_0\rangle = (2\pi)^{-3/2}\chi_{i_0}e^{-\imath\mathbf{k}_0\cdot\mathbf{r}},$$

χ_{i_0} is an internal state wave function and t is only on the enrgy shell when

$$E = \frac{\hbar^2}{2\mu}\mathbf{k}_0^2 + E_{\chi_0}.$$

The partial wave equivalent of the 3-D Lippmann-Schwinger equation[12] is

$$\psi_{li}^+(r \mid i_0k_0E) - u_l(k_0r)\delta_{ii_0} - \int_0^\infty dr'\omega_l^+(k_ir_>)u_l(k_ir_<)\sum_{i'l'}V(r')_{il,i'l'}\psi_{i'l'}^+(r' \mid i_0k_0E)$$

$$\begin{aligned} r_< &= \min(r.r') \\ r_> &= \max(r, r') \end{aligned}$$

and u_l and ω_l^+ are incoming and outgoing spherical Bessel functions. A simple extension of the Sams-Kouri method[12] expresses the solution as

$$\mathbf{C} = -(\mathbf{I} + \mathbf{B}^1)^{-1}\cdot\mathbf{B}^0,$$

$$B_{il,i'l'}^x = \int_0^\infty dr\omega_l^+(k_i^1r)V_{il,i'l'}(r)\psi_{i'l'}^x(r \mid i_0k_0E), \qquad x = 0, 1,$$

where ψ^0 and ψ^1 obey almost identical Volterra equations

$$\omega^x_{il}(r \mid i_0 k_0 E) = u_l(k^x_i r)\delta_{ii_0} + \int_0^r dr'[\omega^+_l(k^1_i r)u_l(k^1_i r') - \varpi^+_l(k^1_i r')u_l(k^1_i r)] \times \sum_{i'l'} V(r')_{il,i'l'}\psi^x_{i'l'}(r' \mid i_0 k_0 E). \qquad x = 0, 1$$

$$k^0_i = [k^2_o + \frac{2\mu}{\hbar^2}(E_i - E_{i_0})]^{1/2} = k_{iin},$$

$$\kappa^+_i = \hbar^{-1}[2\mu(E - E_{i_0})]^{1/2} = k_{iout}.$$

In the original Sams-Kouri treatment, which was restricted to the energy shell, $\mathbf{B}^0 = \mathbf{B}^1$ and $\psi^0 = \psi^1$. Otherwise, except for the necessity of solving two Volterra equations rather than one, everything in the off-energy-shell extension is much the same. The principal advantage of this method is that the replacement of a single set of integral equations of the Fredholm type by two sets of Volterra equations means that when one replaces the integration over a continuum by sums over a discrete set of points; $r_0 < r < r_{\max}$,the value of the auxiliary functions, ψ^x at a point, r, depends only on the solution of the interior points, $r' < r$. The only inversion procedure occurs in the calculation of the matrix, $\mathbf{C}$, which is done after all the integrations. The second advantage is that the coding of this method is surprisingly simple. The main disadvantage, as will appear in thte discussion below, is that when one starts the solution too far into the unclassical region, the solutions become unstable and untrustworthy.

The partial wave t-matrix element then becomes, for no internal degrees of freedom.

$$\left\langle k' \mid t^l(E) \mid k_{in} \right\rangle = (u_l(k'r).V\psi^+(r \mid k_{in}E)).$$

To test the code, the first system tried was the rigid sphere potential on the energy shell, approximated by

$$\begin{aligned} V &= c, && r < r_s \\ &= 0, && r > r_s. \end{aligned}$$

As $c \to \infty$, this potential becomes highly singular for this method if too mnay points are included inside the repulvive core . Algorithms were tested that have been stated to take care of instabilities of Sams-Kouri functions in the non-classical region, but I did not find them especially effective. The only one that seemed to be reasonably useful, *ie* that gave phase shifts agreeing to three places with the rigid sphere value,[13] was to find by trial and error a set of values of the initial point, r_0 , for the final solution, ψ^x was relatively insensitive to r_0.

A second test calculates sample off shell t-matrices for the Hg-H_2 potential used by Brumer and Shapiro[14] and, *cf* Figures 1a and 1b, compares their calculated t-matrices and the modified Sams-Kouri values. These were computed at a single orbital

angular momentum, $\ell = 5$, using the hit or miss method of choosing r_0 outlined in the previous paragraph. The agreement is not perfect, but satisfactory for exploratory calculations.

D. On a conjecture of Roney

To describe the far wings of isolated lines, Roney[10] has developed a perturbation evaluation of the Fano tetradic[11] in which it is implicitly assumed the t-matrix is a smooth and differentiable function, capable of being expanded in a Taylor series. That is, the Fano tetradic involves terms like

$$t_{\mathbf{k'k}} = \langle \mathbf{k'} \mid t(k_E) \mid \mathbf{k} \rangle ,$$

for which the derivatives

$$\frac{\partial}{\partial k'} t_{\mathbf{k'k}} \neq \frac{\partial}{\partial k_E} t_{\mathbf{k'k}} \neq \frac{\partial}{\partial k} t_{\mathbf{k'k}} \neq \left(\frac{d}{dk_E} t_{\mathbf{k'k}} \right)_{k'=k_E=k}$$

are not generally equal - except on the energy shell, *ie* for $dk' = dk_E = dk$ - , there is no one quantity, like the time delay matrix, that relates all four derivatives simply. To illustrate this, calculations were carried out with the Sams-Kouri formalism of all four derivatives. Figures 2a and 2b and 3a and 3b, computed for $\ell = 5$ and $\ell = 12$ for the points on the energy shell, $k' = k_E = k$, show that, at least for the derivatives of the partial wave t-matrices, the four derivatives are not equal. They are not even remotely similar. Implementing Roney's formulation numerically will therefore not be a simple job. Unfortunately, due to the appearance of resonance spikes, it would not be an easy job either. As will be seen from Figures 4a and 4b, the resonance structure is even more marked for several t-matrices displaced from the energy shell by finite distances. This implies that only with due caution should Taylor series expansions of off-shell t-matrix be implemented.

Since it has long been known[14,15,16] that the off-shell t-matrix is an oscillatory of k' and k at constant k_E, it is no surprise that the derivative is also oscillatory. As noted above, what is surprising is that for certain directional derivatives, *ie* $dk' = dk = 0$, resonance like structures are also apparent. This is especially apparent in Figures 4a and 4b where the t-matrix is computed at finite displacements from the energy shell. It seems tempting to relate this to coincidence of favorable and unfavorable phase relationships between ingoing and scattered waves as k', k_E, k are varied. This is a rather interesting phenomenon in itself and should be looked into more closely.

I. References

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FIGURE 1a

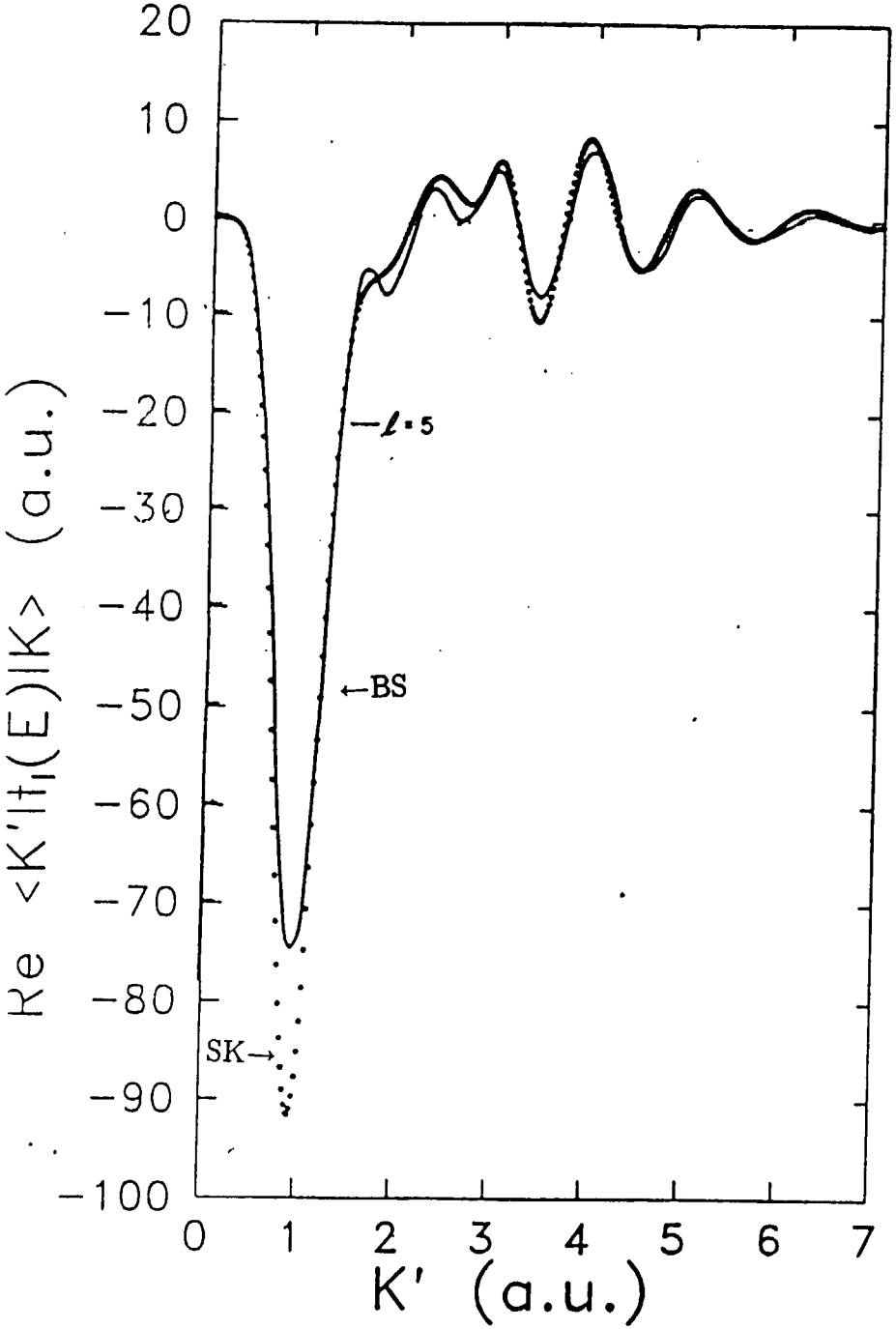


FIGURE 1b

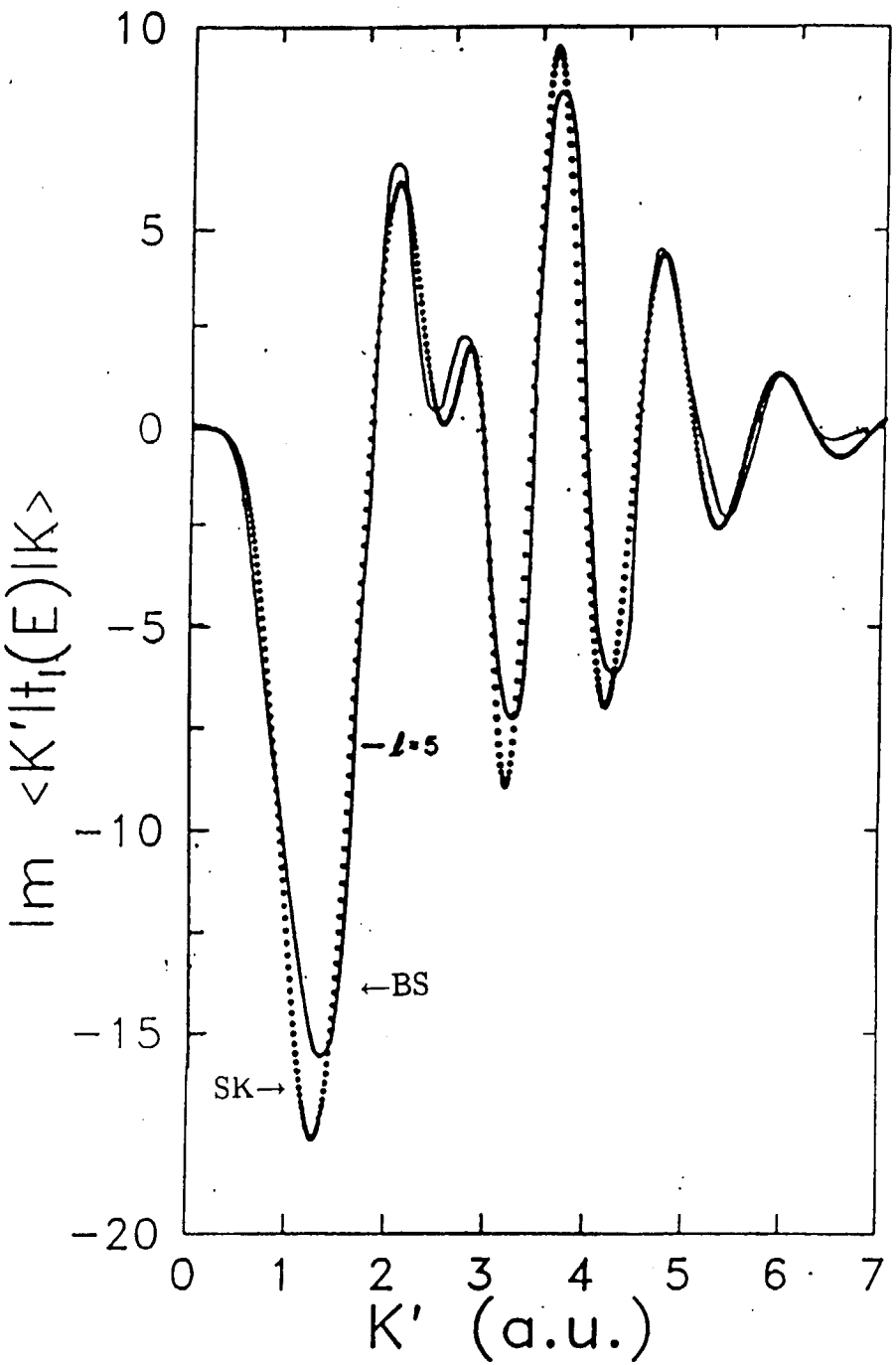
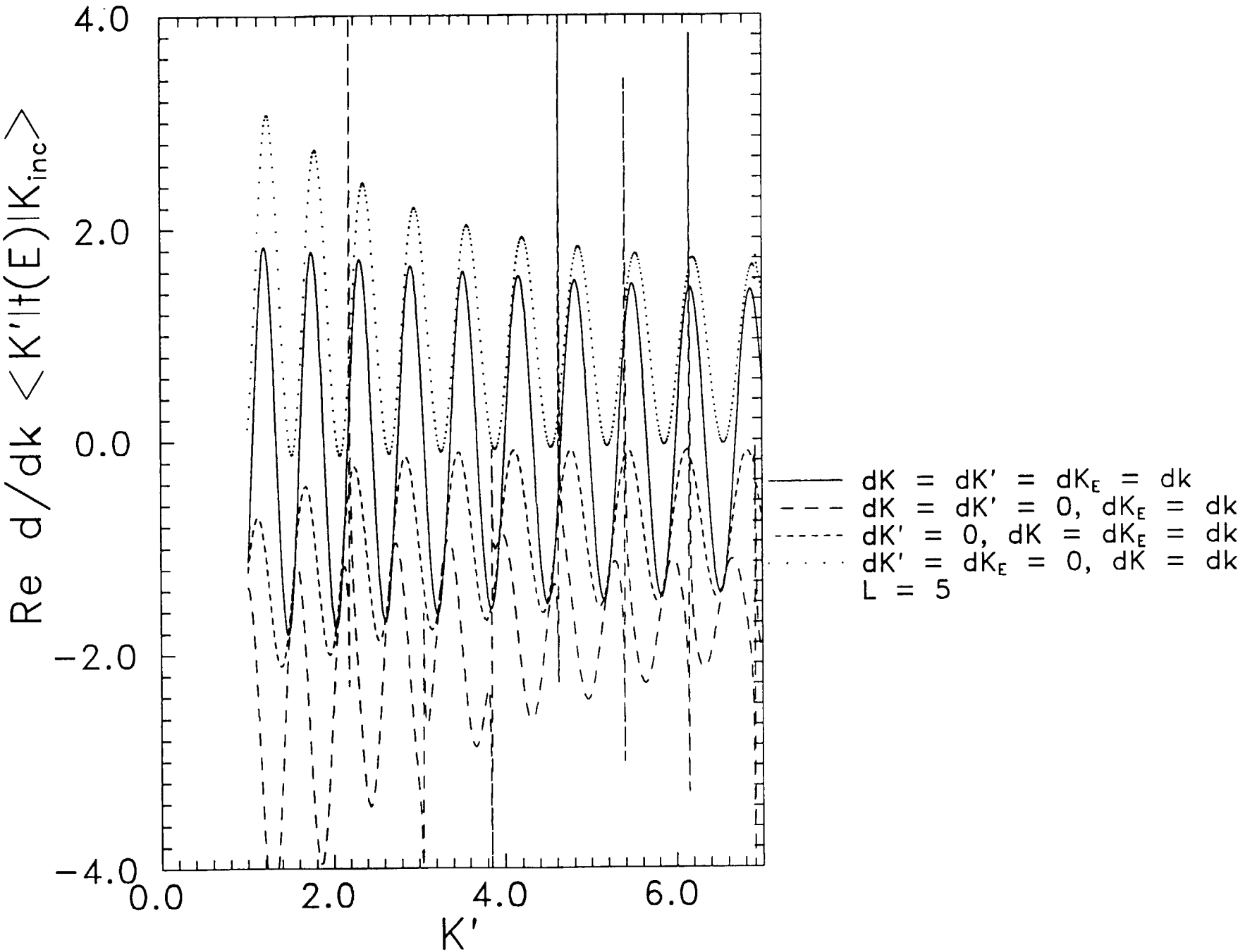


FIGURE 2a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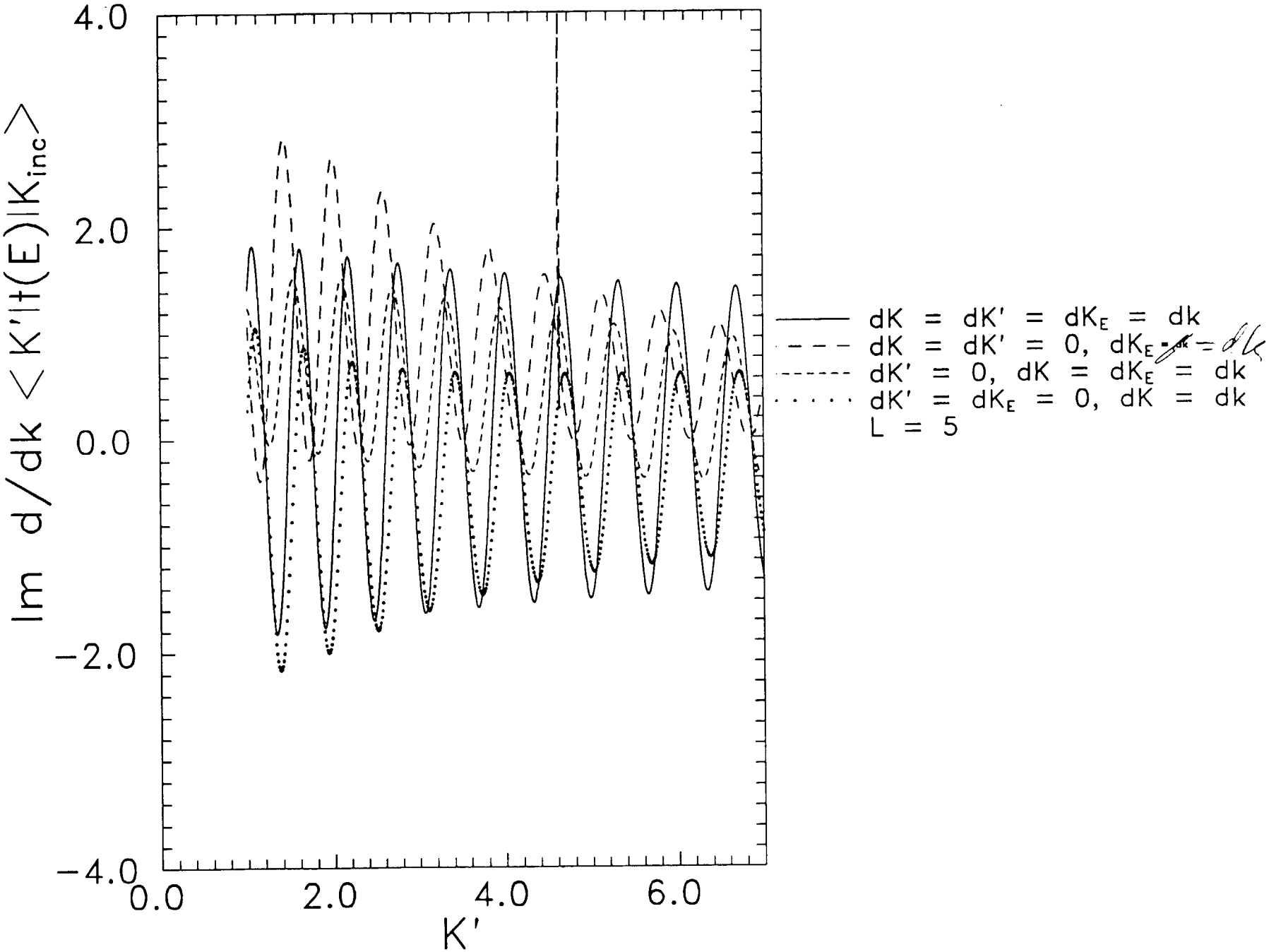
2.0
0.0
−2.0
−4.0
0.0
2.0
4.0
6.0
K'
Re d/dk <K'|t(E)|K_inc>
dK = dK' = dK_E = dk
dK = dK' = 0, dK_E = dk
dK' = 0, dK = dK_E = dk
dK' = dK_E = 0, dK = dk
L = 5

FIGURE 2b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2.0
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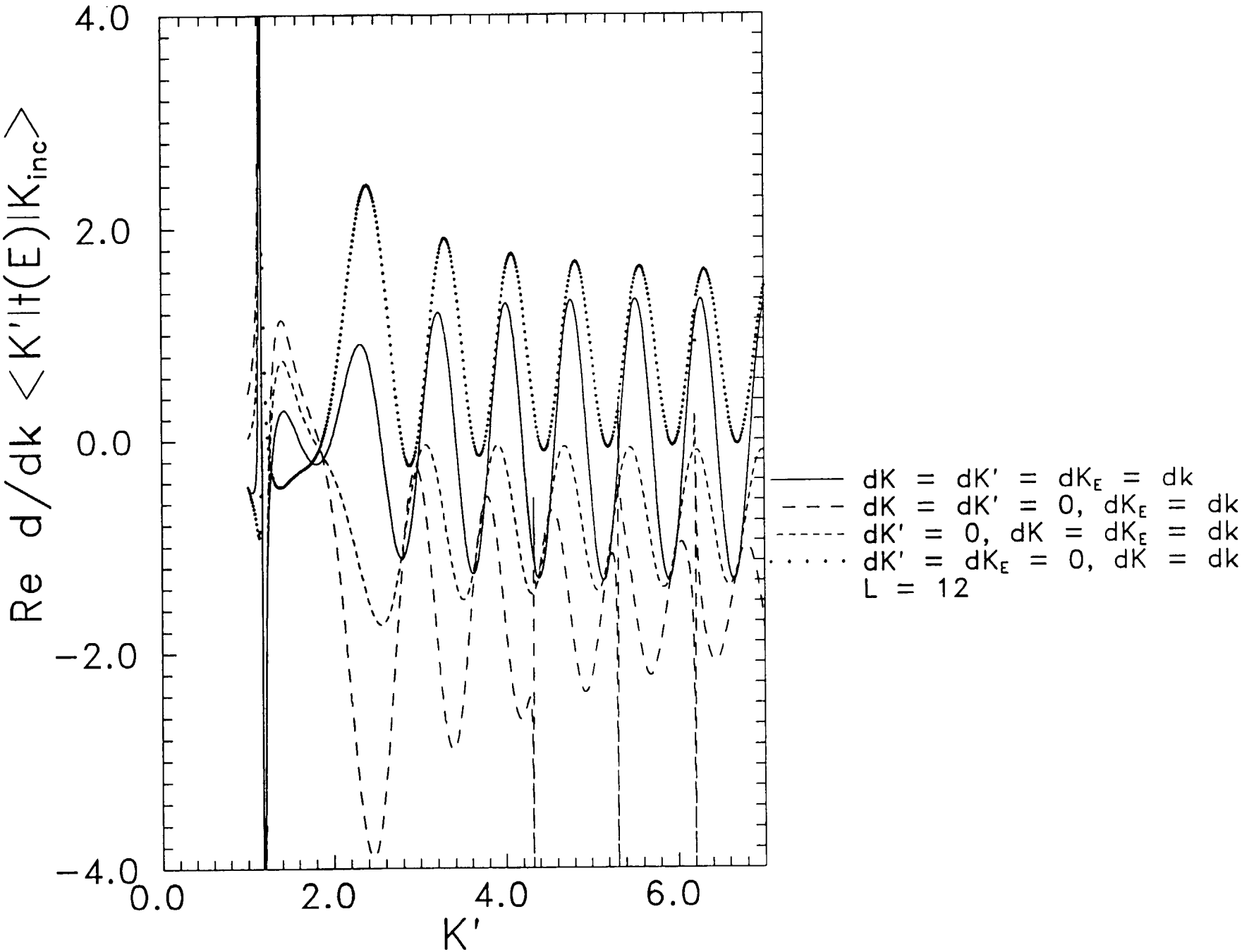
−4.0
0.0
2.0
4.0
6.0
K'
Im d/dk < K'|t(E)|K_inc >
dK = dK' = dK_E = dk
dK = dK' = 0, dK_E = dk
dK' = 0, dK = dK_E = dk
dK' = dK_E = 0, dK = dk
L = 5

FIGURE 3a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K'
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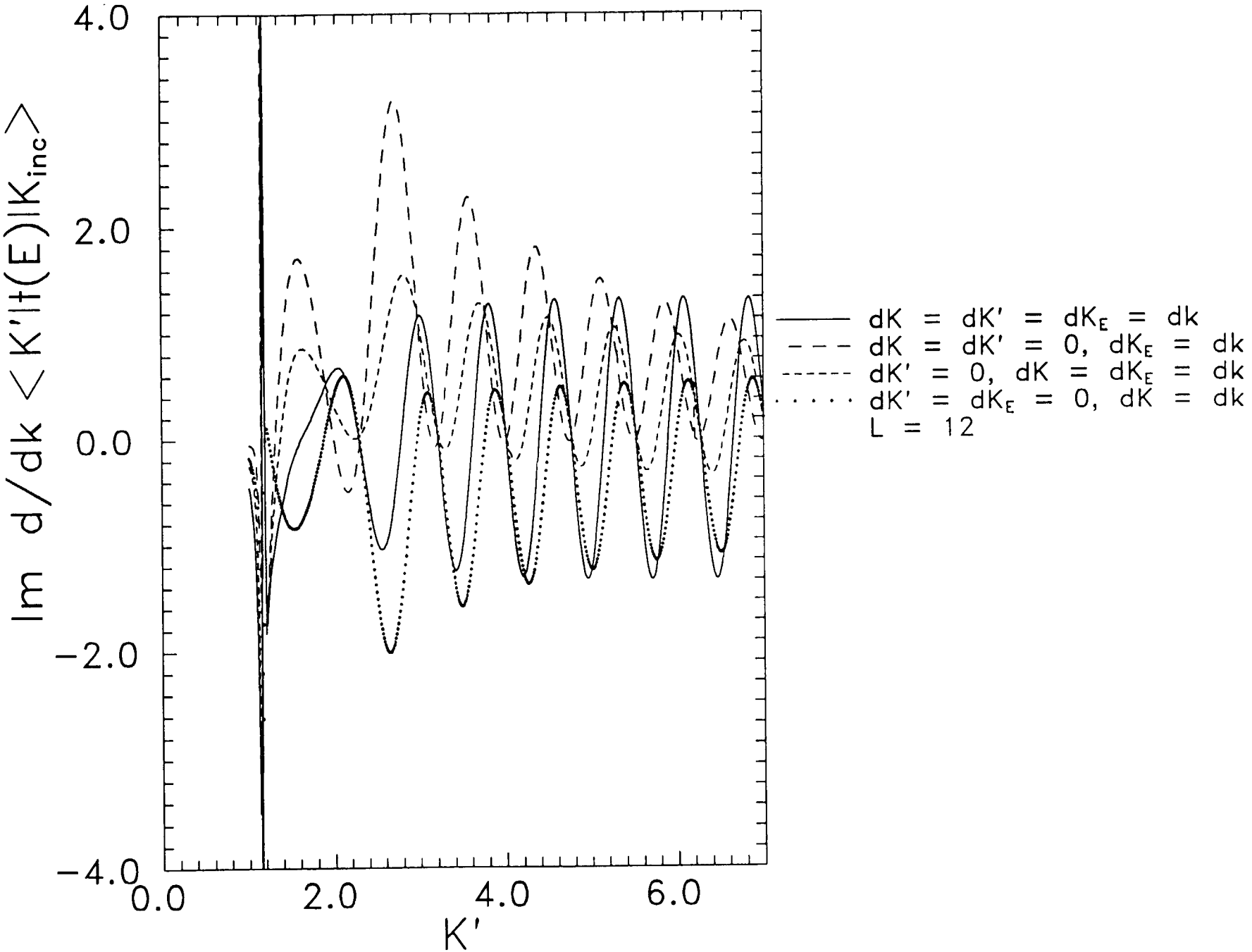
dK = dK' = dK_E = dk
dK = dK' = 0, dK_E = dk
dK' = 0, dK = dK_E = dk
dK' = dK_E = 0, dK = dk
L = 12

FIGURE 3b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−2.0
−4.0
0.0
2.0
4.0
6.0
K'
Im d/dk <K'|t(E)|K_inc>
dK = dK' = dK_ε = dk
dK = dK' = 0, dK_ε = dk
dK' = 0, dK = dK_ε = dk
dK' = dK_ε = 0, dK = dk
L = 12

FIGURE 4a

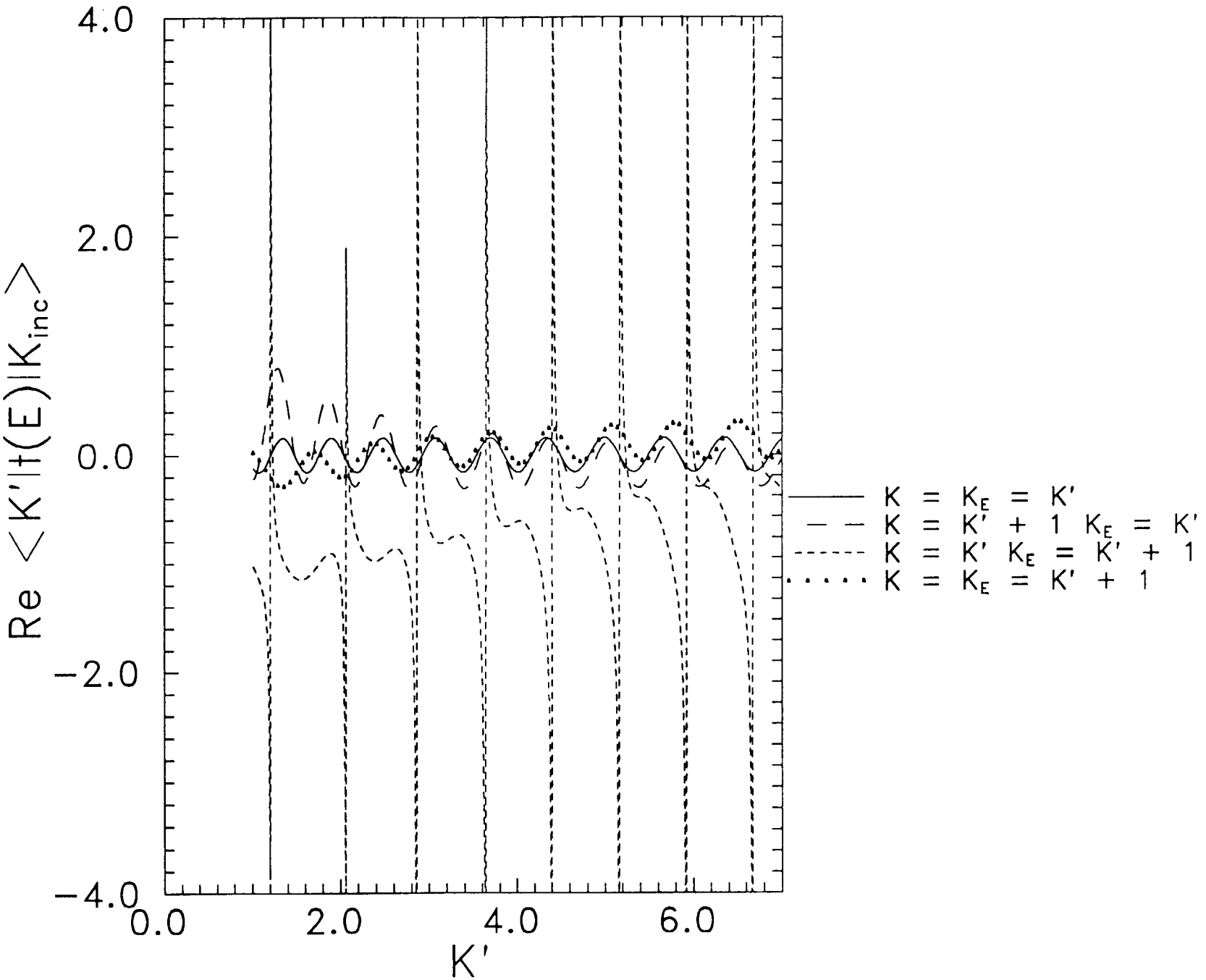

FIGURE 4b